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Syntheses and structural characterizations of phenylimidorhenium(V) complexes containing bi- or tetra-dentate phosphinoamido ligands

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The substitution reaction of [Re(NPh)Cl$_3$(PPh$_3$)$_2$] with H$_2$dpa [(*o*-aminophenyl)diphenylphosphine] led, depending on the solvent polarity, to the formation of the diamagnetic neutral phenylimido complex [Re(NPh)Cl(Hdpa)$_2$] **2** and the monocationic [Re(NPh)Cl(Hdpa)(H$_2$dpa)][ClO$_4$] **4**. Conversely, H$_2$dppd {*N*,*N*′-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine} gave only the cationic compound [Re(NPh)Cl(Hdppd)]Cl **6**, where the ligand is uninegative. In alkaline alcohols, the neutral complexes [Re(NPh)(OMe)(Hdpa)$_2$] **1** and [Re(NPh)(OEt)(dppd)] **5** were obtained. The reaction of H$_2$dpa in a 1 : 1 ligand to precursor ratio produced the monosubstituted complex [Re(NPh)Cl$_3$(H$_2$dpa)] **3**. The compound [Re(NPh)Cl(Hdpa)$_2$] can also be prepared by treating for several hours in refluxing xylene the isostructural oxo complex [ReO(Cl)(Hdpa)$_2$] and aniline. All the complexes are stable in the solid state, however those containing the bidentate ligand show instability, in particular in chlorinated solvents. This is discussed in terms of the different π-donation abilities of the amide, alkoxide and chloride ligands. Despite a predicted number of electrons largely exceeding 18, the crystal structure determinations for **1**, **2** and **5** do not show significant deviation from linearity of the Re–N–Ph moiety, but only an unusual elongation of the Re–OR (R = Me or Et) bonds in **1** and **5**. The NMR and structural data are compared with those of oxo analogues previously reported.

Phosphinoamine chelating ligands possess good co-ordination abilities by virtue of the combined σ–π donor–acceptor properties of the P,N co-ordination set. The reactivity of (*o*-aminophenyl)diphenylphosphine (H$_2$dpa) and its derivative, *N*,*N*′-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine (H$_2$dppd) toward Re, Tc and Cu[1–6] has been extensively studied by our research group. Series of oxo and nitrido complexes of Tc and Re have been prepared. In general, two bidentate ligands or a tetradentate one, variously protonated, are co-ordinated to the metal along with auxiliary ligands such as RO$^-$ and X$^-$ (R = Me, Et, MeCO, *etc.*; X = Cl, Br or I)[2,5] in octahedral environments. Particular synthetic conditions allow double deprotonation of the primary amino group of one chelate producing the stable octahedral rhenium(V) complex [Re(dpa)Cl$_2$(Hdpa)],[6] which contains an unusual bent imido moiety.

While a considerable number of six-co-ordinated rhenium complexes, incorporating a linear Re≡N–R unit (N, 4e$^-$ donor), has been prepared,[7–11] few cases containing a significantly bent imidorhenium moiety (N, 2e$^-$ donor) have been reported.[12] The effective atomic number (EAN) rule, which is often obeyed by a metal such as rhenium,[6] predicts that when the formal electron count exceeds the usual 18 the nitrene ligand can bend.[12] However, in the complex [Re(dpa)Cl$_2$(Hdpa)][6] the bent configuration of the imido unit is consistently enforced by the intrinsic ligand geometry and the other ligands which contribute, *via* π-back bonding, to the 18-electron total valence count. Our interest in this work was to prepare phosphinoamidorhenium(V) complexes containing a 'free to bend' phenylimido moiety and evaluate its extent of bending in the presence of the 'electron congestion' originated by the concomitant co-ordination of strong π-donor ligands such as uninegative amido and alkoxo groups.

Recently, high-valent organoimido complexes of Tc and Re have been proposed as potential radiopharmaceuticals as alternatives to oxo and nitrido compounds owing to the possibility of incorporating specific targeting molecules on the substituents at the nitrogen site.[13]

Results and Discussion

The substitution reaction of [Re(NPh)Cl$_3$(PPh$_3$)$_2$] with 2 mol of H$_2$dpa in non-polar solvents (benzene or toluene) leads to the formation of the diamagnetic neutral phenylimido complex [Re(NPh)Cl(Hdpa)$_2$] **2**. Conversely, in polar solvents (MeOH, EtOH or MeCN) the monocation [Re(NPh)Cl(Hdpa)(H$_2$dpa)][ClO$_4$] **4** is produced, in which one of the ligands is bonded as a neutral donor. Complex **2** can be converted into **4** by addition of NaClO$_4$ dissolved in CH$_2$Cl$_2$–MeOH (20 : 80).

The reaction of H$_2$dppd with the precursor [Re(NPh)Cl$_3$(PPh$_3$)$_2$] in acetonitrile gives the compound [Re(NPh)Cl(Hdppd)]Cl **6**, where the phosphinoamine ligand is uninegative. In alkaline alcohols H$_2$dpa and H$_2$dppd yield the neutral complexes [Re(NPh)(OMe)(Hdpa)$_2$] **1** and [Re(NPh)(OEt)(dppd)] **5**, respectively. Finally, the monosubstituted complex [Re(NPh)Cl$_3$(H$_2$dpa)] **3** is obtained by performing the reaction with a 1 : 1 ligand to precursor ratio; this complex contains one neutral bidentate ligand.

The syntheses of all these complexes do not require either anhydrous solvents or any controlled atmosphere, however, due to the low solubility of the rhenium precursors, reflux temperatures are necessary. Interestingly, the complex [Re(NPh)Cl(Hdpa)$_2$] can be synthesized also by treating the isostructural oxo-complex [ReO(Cl)(Hdpa)$_2$][2] and aniline, for several hours, in refluxing xylene with a procedure identical to that reported for the syntheses of other phenylimidorhenium(V) species containing π ligands.[11,14] Such a core replacement does not occur in the case of the oxo complex [ReO(OMe)(Hdpa)$_2$].[2]

In general, these phenylimidorhenium(V) compounds are stable in the solid state and in solutions of common solvents, however those derived from H$_2$dppd are unstable and decompose in chlorinated solvents.

As frequently observed for other phenylimidorhenium(V) complexes,[7,11,12] it is extremely difficult to identify the Re–NPh stretches in the IR spectra as they may be mixed with ν(C–N) and ν(P–C) modes of the ligands. In the region 1000–1300

Table 1 Selected spectroscopic properties of complexes **1**–**6**

	IR (cm^{-1})			^1H NMR (δ)		
Complex	ν(N–H)	C–H	^{31}P NMR (δ)	N	Alkyl	Aromatic
1 [Re(NPh)(OMe)(Hdpa)$_2$][a]	3300, 3321	2900–2790	13.9 (s)	8.33 (s)	3.04 (t)	6.4–7.6 (14 H)
2 [Re(NPh)Cl(Hdpa)$_2$][a]	3336, 3263	—	18.0 (m), 17.3 (m)	8.97 (s)	—	6.1–7.9 (14 H)
3 [Re(NPh)Cl$_3$(H$_2$dpa)][b]	3267, 3150, 3122, 1543[c]		5.5 (s)	5.00 (br s, 2 H)	—	7.0–7.6 (14 H)
4 [Re(NPh)Cl(Hdpa)(H$_2$dpa)][ClO$_4$]	3348, 3290		n.d.	n.d.	n.d.	n.d.
5 [Re(NPh)(OEt)(dppd)][d]	—	2958–2706	10.2 (s)	—	3.67 (m, 4 H), 3.06 (qnt, 2 H), 1.95–2.41 (2 H), 0.30 (t, 3 H)	6.4–7.6 (28 H)
6 [Re(NPh)Cl(Hdppd)]Cl[b]	3400 (br)	2942–2721	13.4 (m), 0.5 (m)	5.80 (br s)	5.00–1.40 (8 H)	6.5–7.8 (28 H)

Multiplicity in parentheses: s = singlet, d = doublet, t = triplet, m = multiplet, qnt = quintet, br = broad, n.d. = not detectable. [a] NMR in CD_3CN. [b] NMR in $CDCl_3$. [c] NH_2 bending. [d] NMR in CD_2Cl_2.

cm^{-1}, where the ν(Re–NPh) stretching is expected, only the alkoxo complexes display a significant medium intensity band, at 1068 and 1052 cm^{-1} for [Re(NPh)(OMe)(Hdpa)$_2$] and [Re(NPh)(OEt)(dppd)], respectively. These bands are also detectable in the spectra of analogous oxo complexes.[2,5] Most of the complexes (Table 1) show distinguishable ν(N–H) stretches in the region 3348–3122 cm^{-1}. In particular, two distinct absorptions are present at 3300 and 3321 cm^{-1} for [Re(NPh)(OMe)(Hdpa)$_2$], whereas for [Re(NPh)Cl$_3$(H$_2$dpa)] three medium-intensity bands are located at 3267, 3150 and 3122 cm^{-1}, the last two attributable to the symmetric N–H stretching. Moreover, at 1543 cm^{-1}, the latter compound shows the N–H bending.

As found for the analogous oxo derivatives,[2] FAB$^+$ mass spectrometry shows for all compounds the ion derived by loss of the coligand (Cl^- or ^-OR), whereas the spectrum of [Re(NPh)Cl$_3$(H$_2$dpa)] displays peaks due to sequential loss of two of the three chloride ligands.

Addition of the bulky $[ClO_4]^-$ anion to a methanol solution of complex **2** induces protonation of one of the bidentate ligands, yielding to the cationic complex **4**. Hence, the behaviour of this phenylimido derivative is, to some extent, in between that of the isostructural oxo complex [ReO(Cl)(Hdpa)$_2$] and that of the nitrido one [ReN(Cl)(H$_2$dpa)$_2$]Cl, which contain the monoanionic or the neutral form of the phosphinoamine ligand, respectively.[2,6]

A preliminary electron count for the compound [Re(NPh)Cl(Hdpa)$_2$] **2** indicates that the simultaneous presence of two π-donor amido groups and a linear four-electron donor phenylimido unit supplies an excess of electron density (EAN rule[7] gives a value of 22 electrons if the amido N is assumed to be a $3e^-$ donor[6]). To decrease its electron count the complex may (*i*) bend the phenylimido core, to lower its donor capacity, (*ii*) protonate the amido nitrogen, giving an overall positive charge and (*iii*) decrease π donation from the amido and chloride ligands. The structure of **2** does not show an appreciable bending of the phenylimido unit, at least in the solid state; however, once dissolved in protic solvents, the complex rearranges to a protonated cationic species (**4**), isolated as the perchlorate salt. The formulation of **4** has been assessed by elemental analyses and conductivity measurements (which confirm the 1 : 1 electrolytic nature). Also IR spectroscopy indicates the presence of the ν_3 vibration mode of the $[ClO_4]^-$ anion, at 1092 cm^{-1}.[15] The neutral compound **2** is always isolated if other anions, such as Cl^-, PF_6^- and BF_4^-, are added to the reaction mixture. The acid–base comportment of complexes **2** and **4** is not exhibited by the 'planar' complex [Re(NPh)(OMe)(Hdpa)$_2$] which, in spite of giving its conjugate acid form, by addition of diluted HCl, prefers to convert into the chloride salt of complex **4**. Alkoxo groups are known as good π-donor ligands, indeed structural data often suggest they are able to form double bonds, hence behaving as three-electron donor ligands.[7] In the complex [Re(NPh)(OMe)(Hdpa)$_2$], in order to diminish its donor ability to some extent, the methoxo group must be kept at a distance [2.026(8) Å] greater than the values reported in other similar rhenium(V) arylimido complexes {1.895(5) and 1.948(4) Å for [Re(NPh)(OEt)(bipy)$_2$]$^{2+}$ and [Re(NTol)(OEt)(S$_2$CNMe$_2$)$_2$] (Tol = tolyl), respectively}.[11,12] This description fits well with the fact that in monoimido complexes with maximum electron count (MEC) exceeding 18 electrons the imido core exerts a noticeable *trans* influence.[7] However, this apparently contrasts with a quite long Re–N(2)Ph bond [1.736(9) Å] and the almost linear [175.4(9)°] C(7)–N(2)–Re angle which formally accounts for a N(2)–Re bond order of three. Consequently, the excess of electron density in the linear PhN–Re–OMe moiety is redistributed by π donation, to the equatorial N,P atoms. Phosphorus atoms, being better π acceptors than amido nitrogens, form shorter Re–P bonds when compared with the analogous oxo complex [2.432(2) *vs.* 2.494(3) Å].[2] Likewise, the higher stability of the 'twisted' complex [Re(NPh)Cl(Hdpa)$_2$] may be understood in terms of lower π-donation ability of both the axial amido nitrogen and the equatorial chloride. Moreover, the higher orbital symmetry of the PhN–Re–N moiety, when compared with PhN–Re–OMe, may further contribute to a better electron delocalization.

The complexes with the tetradentate ligand H$_2$dppd show a similar trend of stability: 'planar' [Re(NPh)(OEt)(dppd)], when treated with HCl in acetonitrile, rearranges to protonated 'twisted' [Re(NPh)Cl(Hdppd)]Cl which is stable also in chloroform solutions.

Proton NMR spectra of the phenylimido complexes (Table 1) confirm that their structures in solution are identical to those found in the solid state. Thus, the aromatic region containing signals from protons of the phenyl groups of the imido and phosphorus donors is accompanied by distinctive signals corresponding to amino, amido and/or alkyl protons. In particular, amido protons of equatorially co-ordinated P,N chelates fall downfield (*e.g.* in complexes **1** and **2**), beyond the aromatic region, whereas amine protons (in complex **3**) and amido ones, located *trans* to the phenylimide (in complexes **2** and **6**), fall upfield in the δ 5.00–5.80 region. A similar shielding effect is experienced by the alkyl protons of the alkoxo group in complexes **1** and **5** (Table 1). These signals are shifted remarkably upfield when compared to those of the free alcohols, but significantly less shielded than the corresponding signals arising from isostructural oxorhenium complexes [ReO(OMe)(Hdpa)$_2$] (δ_{OMe} 2.74) and [ReO(OEt)(dppd)] [δ_{OEt} 2.56 (CH$_2$) and 0.15 (CH$_3$)]. These data indicate a less pronounced electron transfer from the imido core to its *trans* coligand than that exerted by the oxo moiety. Concomitantly, amido protons are far less deshielded in phenylimido complexes than in oxo analogues, indicating a stronger contribution of the equatorial donors to the overall stability of the former class of compounds. The ^{31}P NMR spectra distinguish between 'equatorial' and 'twisted' molecular

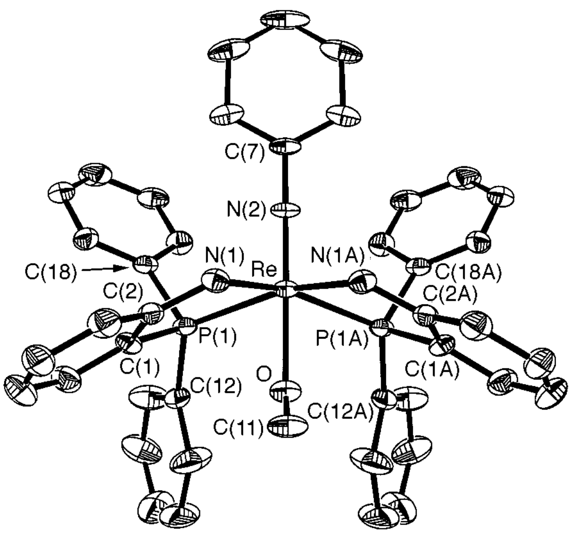

Fig. 1 An ORTEP[16] view of complex **1** with 40% probability ellipsoids. The H atoms have been omitted for clarity

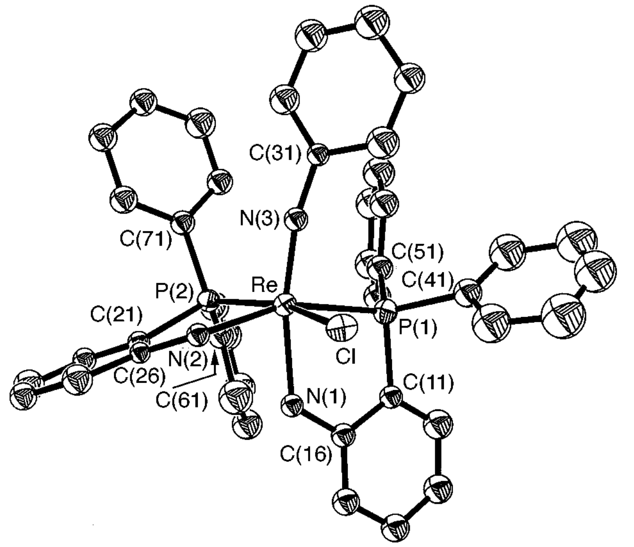

Fig. 2 An ORTEP view of complex **2** with 40% probability ellipsoids

structures giving a sharp singlet and two multiplets, respectively. In the latter case (complexes **2** and **6**) the increased multiplicity is accounted for by the magnetic inequivalence of the *cis*-positioned phosphorus donors (see also X-ray analysis). Moreover, the spectra of all the phenylimido complexes show ^{31}P chemical shifts which fall downfield with respect to those of the oxo analogues. This behaviour is consistent with a stronger Re–P interaction in the phenylimido complexes.

Crystal structures

The three monomeric, neutral and octahedral phenylimido complexes **1**, **2** and **5** (Figs. 1–3) are formally rhenium(V) species, with the phenylimido unit formally a dianionic ligand. In **1** the co-ordination of the two bidentate $Hdpa^-$ uninegative chelates occurs symmetrically in the equatorial plane orthogonal to the imidorhenium direction, with a mutual *cis*-phosphorus configuration, in a mode designed as 'equatorial' by Refosco *et al.*[2] The site *trans* to the phenylimido unit is occupied by a methoxide ligand. In **2** the two mutually orthogonal $Hdpa^-$ chelates co-ordinate the rhenium while still preserving the *cis*-phosphorus configuration, one ligand bridging an equatorial and an apical position (with the phosphinoamido nitrogen *trans* to the imido unit) and the other two equatorial sites ('twisted' mode). A chloride atom completes the equatorial plane. In **5** the tetradentate P_2N_2-dianionic ligand occupies the four positions of the equatorial plane orthogonal to the imidorhenium axis, with an ethoxide ligand at the other axial position. The crystal structure of **5** consists of two independent and well separated moieties (A and B) and a water molecule is trapped, without any significant interaction. The structures of A and B are roughly superimposable: the weighted root-mean-square (r.m.s.) deviation, derived by the BMFIT program,[17] is 0.09 Å, when the fitting is performed using the 13 nearest atoms to Re (Fig. 4). However, the two units differ in the periphery. In particular, the major differences reside in the orientation of the phenylimido ring relative to the equatorial mean plane (dihedral angle 73.4° in A and 81.8° in B), and in the orientation of the O(1)–C(22)–C(23) plane with respect to the P_2N_2 mean plane (dihedral angle 65.5° in A and 91.1° in B), along with the relative orientation of the four phenyl rings at P(1) and P(2).

Some common features can be found in the three complexes. (*i*) The Re^V lies out of the mean equatorial plane (by 0.34, 0.26 and 0.31 Å in **1**, **2** and **5**, respectively). (*ii*) In the equatorial co-ordination mode the P_2N_2 atoms are all bowed slightly away from the phenylimido moiety to minimize steric congestion around the rhenium atom and the dihedral angles between the phenyl 'wings' are 59.6, 58.1 and 54.5° in **1**, **5A** and **5B**, respectively. (*iii*) Around the metal the RePCCN five-membered rings adopt a twist-envelope (C_2) conformation when the co-ordination mode is equatorial (torsion angles ranging from −20.6 to 20.2°), while the conformation is virtually planar in the 'twisted' mode of **2** (torsion angle in the range from −3.9 to 2.8°). On the other hand, in the six-membered ring of **5** the conformation is a boat, with Re and C(8) atoms deviating from the P(1)C(7)C(9)P(2) mean plane by 0.51 and 0.74 Å, respectively. (*iv*) The phenylimido moiety is roughly perpendicular to the mean equatorial plane (dihedral angles 95.2, 82.6, 73.4 and 81.8° in **1**, **2**, **5A** and **5B**, respectively). (*v*) As observed by Nicholson *et al.*[18] for technetium(V) phenylimido complexes, the phenyl rings at P(1) and P(2) atoms are angled towards the phenylimido core, forming a pocket around the nitrogen atom. A comparison of **1** with the dication complex *trans*-$[Re(NPh)(OEt)(bipy)_2]^{2+}$[11] emphasizes two features: (*a*) although the Re–NPh bond is 1.74 Å in both complexes, the Re–OEt distance [1.895(5) Å] reflects some multiple-bond character undetectable in **1** [Re–OMe 2.026(8) Å]; (*b*) the angles in the Ph–N–Re–O moiety seem to be correlated in that as the Ph–N–Re approaches 180° the N–Re–O angle deviates from linearity (and *vice versa*). In particular, in **1** the pertinent angles are 175.4(9) and 166.2(4)°, while in the dicationic complex the corresponding values are 167.4(6) and 174.8(3)°.

Bond lengths and angles within the inner core show no unusual features, being within the range expected from the comparison of other six-co-ordinated rhenium(V) complexes containing similar ligands.[2,5] Therefore, the Re–N–C bond angle [175.4(9), 168(2), 169.8(9) and 174.3(9)° in **1**, **2**, **5A** and **5B**, respectively, Table 2] confirms the linear co-ordination mode of the triply bonded phenylimido unit and the Re–N distance [1.736(9), 1.72(2), 1.73(1) and 1.76(1) Å] agrees with the values found in the other phenylimidorhenium complexes (Table 3). The Re–N distance seems to be unaffected by the oxidation number and the geometry about Re; its mean value (1.735 Å) is only 0.03 Å greater than that found in similar technetium complexes.[18] Since the imido core RN^{2-} is formally isoelectronic to the oxo core O^{2-} and tends to form analogous Group 7 co-ordination complexes, comparison of **1**, **2** and **5** with $[ReO(OEt)(Hdpa)_2]$,[2] $[ReO(Cl)(Hdpa)_2]$[2] and [ReO(OMe)(dppd)],[5] respectively, deserves comment. The structures of the analogous phenylimido- and oxo-rhenium(V) complexes are substantially superimposable, the average r.m.s. deviation being 0.10 Å when the fitting is performed using the octahedron atoms. For example, for $[Re(NPh)(OMe)(Hdpa)_2]$ **1** and $[ReO(OEt)(Hdpa)_2]$[2] (r.m.s. 0.09 Å) an apparent diversity, apart from the relative orientation of the phenyl rings, is the larger

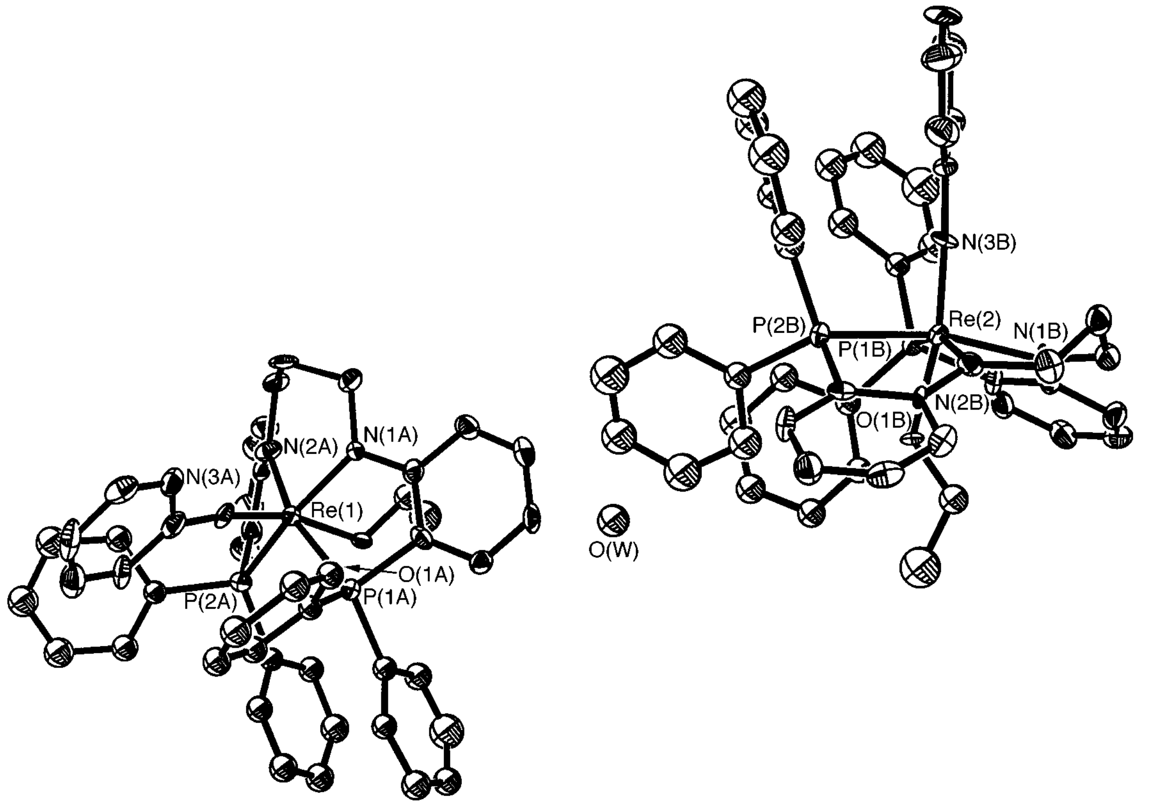

Fig. 3 Relative orientation of the two molecules in the asymmetric unit of complex **5**. Details as in Fig. 1

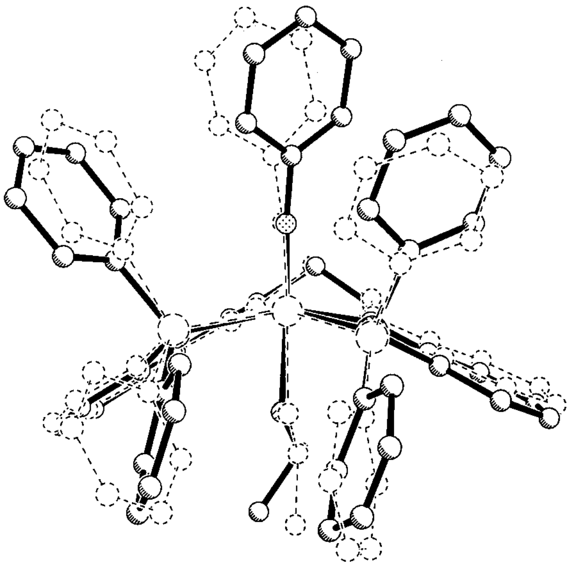

Fig. 4 Superimposition of molecules A (——) and B (----) of complex **5**

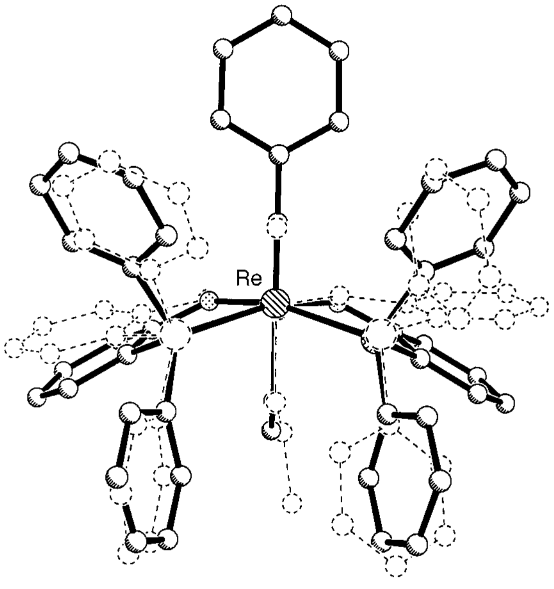

Fig. 5 Superimposition of structures **1** and [ReO(OEt)(Hdpa)$_2$] (----)

'umbrella' bend of the phenylimido ligand (Fig. 5). Finally, the slight difference in the Re–P bond lengths is also perceivable at ^{31}P NMR level (see above).

Experimental

Physical measurements and materials

Elemental analyses (C, H, N) were performed on a Carlo Erba model 1106 elemental analyser. The IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000–400 cm^{-1}) using KBr pellets, ^{1}H and ^{31}P NMR spectra on a Bruker AC-200 instrument, using SiMe$_4$ (^{1}H) as internal reference and 85% aqueous H_3PO_4 (^{31}P) as external reference, and UV/VIS spectra in CH_2Cl_2 using a Cary 17D spectrophotometer (800–250 nm). Conductivity measurements were made at 25 °C using a Metrohm Herison E518 conductimeter. Fast-atom bombardment mass spectra in the positive mode (FAB$^+$) were recorded by using a 3-nitrobenzyl alcohol matrix on a VG ZAB-2F spectrometer. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV (eV $\approx 1.60 \times 10^{-19}$ J). Data were collected over the mass range 100–1000 at 0.7 s per scan.

Unless otherwise stated, all chemicals and solvents were of reagent grade. The complex [Re(NPh)Cl$_3$(PPh$_3$)$_2$] was prepared as previously reported,[27] as were H$_2$dpa[28] and H$_2$dppd.[29]

Syntheses

[Re(NPh)(OMe)(Hdpa)$_2$] 1. In a round-bottomed flask were mixed solid [Re(NPh)Cl$_3$(PPh$_3$)$_2$] (136 mg, 0.15 mmol) and solid H$_2$dpa (83 mg, 0.3 mmol); to the mixture an alkaline [by NEt$_3$

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **5**

1

Re–P(1)	2.432(2)	P(1)–C(1)	1.82(1)
Re–N(1)	2.014(7)	N(1)–C(2)	1.36(1)
Re–N(2)	1.736(9)	N(2)–C(7)	1.40(1)
Re–O	2.026(8)		
P(1)–Re–N(1)	78.7(2)	O–Re–N(1)	86.7(3)
P(1)–Re–N(2)	95.4(2)	N(1)–Re–N(1A)	86.6(4)
P(1)–Re–O	76.9(1)	O–Re–N(2)	166.2(4)
P(1)–Re–P(1A)	110.3(1)	Re–N(2)–C(7)	175.4(9)
P(1)–Re–N(1A)	158.5(2)	Re–P(1)–C(1)	98.7(3)
N(1)–Re–N(2)	103.3(3)	Re–N(1)–C(2)	125.1(5)

2

Re–Cl	2.465(6)	Re–N(1)	2.06(2)
Re–P(1)	2.441(6)	Re–N(2)	2.04(2)
Re–P(2)	2.416(6)	Re–N(3)	1.72(2)
P(1)–C(11)	1.80(2)	P(2)–C(21)	1.79(2)
P(1)–C(41)	1.83(2)	P(2)–C(61)	1.82(1)
P(1)–C(51)	1.80(1)	P(2)–C(71)	1.82(1)
N(3)–C(31)	1.36(3)		
Cl–Re–P(1)	95.2(2)	P(2)–Re–N(1)	87.0(5)
Cl–Re–P(2)	162.8(2)	P(2)–Re–N(2)	81.3(5)
Cl–Re–N(1)	87.5(5)	P(2)–Re–N(3)	97.5(6)
Cl–Re–N(2)	81.8(5)	N(1)–Re–N(2)	82.2(7)
Cl–Re–N(3)	91.0(5)	N(1)–Re–N(3)	168.3(7)
P(1)–Re–P(2)	99.5(2)	N(2)–Re–N(3)	109.1(7)
P(1)–Re–N(1)	77.9(5)	Re–N(3)–C(31)	168(2)
P(1)–Re–N(2)	159.9(5)	Re–N(1)–C(16)	125(1)
P(1)–Re–N(3)	90.7(5)	Re–N(2)–C(26)	122(1)

5

	Molecule A	Molecule B
Re–P(1)	2.425(4)	2.424(4)
Re–P(2)	2.412(4)	2.434(4)
Re–O	2.001(8)	2.005(8)
Re–N(1)	2.06(1)	2.10(1)
Re–N(2)	2.09(1)	2.07(1)
Re–N(3)	1.73(1)	1.76(1)
N(1)–C(2)	1.39(2)	1.32(2)
N(2)–C(11)	1.32(2)	1.38(2)
N(3)–C(16)	1.40(2)	1.34(2)
P(1)–Re–N(1)	79.6(3)	80.0(3)
P(2)–Re–N(2)	77.9(3)	78.8(3)
P(1)–Re–P(2)	106.7(1)	106.4(1)
N(1)–Re–N(2)	91.1(5)	90.9(4)
O–Re–N(3)	165.3(4)	168.2(4)
P(1)–Re–N(3)	91.1(3)	96.9(3)
P(2)–Re–N(3)	95.0(4)	92.2(4)
N(1)–Re–N(3)	103.8(5)	100.2(5)
N(2)–Re–N(3)	104.7(5)	101.9(4)
Re–N(1)–C(2)	121.8(9)	123.0(9)
Re–N(2)–C(11)	121.1(9)	121.7(8)
Re–N(3)–C(16)	169.8(9)	174.3(9)

(707 mg, 7 mmol)] methanol solution (15 cm^3) was added. The green suspension was refluxed for 2.5 h and the final brown solution reduced in volume by flowing through a dinitrogen stream. The red-brown solid was filtered off, washed with aliquots (2 × 1.5 cm^3) of MeOH followed by diethyl ether (3 cm^3). Yield 100 mg, 77% (Found: C, 58.6; H, 4.1; N, 4.4. $C_{43}H_{38}N_3OP_2Re$ requires C, 59.99; H, 4.45; N, 4.88%). The complex is soluble in dichloromethane, chloroform (with decomposition), acetone and acetonitrile, slightly soluble in ethanol, methanol and diethyl ether and insoluble in hydrocarbons. FAB$^+$ mass spectrum: *m*/*z* 830 ([*M* − OMe]$^+$, 100%). UV/VIS: λ_{max} 424 (ε 9400) and 343 nm (13 100 dm^3 mol^{-1} cm^{-1}). X-Ray-quality crystals were obtained from a dichloromethane solution layered with methanol.

[Re(NPh)Cl(Hdpa)$_2$] 2. *Method* 1, *from* [*Re*(*NPh*)*Cl*$_3$(*PPh*$_3$)$_2$]. The complex [Re(NPh)Cl$_3$(PPh$_3$)$_2$] (154 mg, 0.17 mmol) was suspended in benzene (10 cm^3) and solid H$_2$dpa (94 mg, 0.34 mmol) was added. The green mixture was refluxed for 10 h, under a dinitrogen atmosphere, until the green solid was dissolved and for 10 h to produce a brown-red solution. On cooling the solution gave a violet-brown solid which was washed twice with portions of benzene (2 cm^3) followed by diethyl ether (3 cm^3) and dried under vacuum. A further amount of product was recovered from the filtrate by concentration to an oil (2 cm^3) and treatment with acetonitrile (5 cm^3). This solid was washed as for the main crop. Total yield 118 mg, 80% (Found: C, 58.2; H, 4.1; N, 4.5. $C_{42}H_{35}ClN_3P_2Re$ requires C, 58.30; H, 4.08; N, 4.86%). The complex is soluble in dichloromethane, chloroform (with decomposition), acetone and acetonitrile, slightly soluble in benzene and diethyl ether and insoluble in hydrocarbons. FAB$^+$ mass spectrum: *m*/*z* 830 ([*M* − Cl]$^+$, 100%). UV/VIS: λ_{max} 468 (ε 11 100), 433 (11 800) and 330 nm (16 800 dm^3 mol^{-1} cm^{-1}). Crystals suitable for the X-ray determination were grown from a dichloromethane solution layered with diethyl ether.

Method 2, *from* [*ReO*(*Cl*)(*Hdpa*)$_2$]. The complex [ReO(Cl)(Hdpa)$_2$] (40 mg, 0.05 mmol) was dissolved in xylene (15 cm^3) and aniline (19 mg, 0.2 mmol) added. The mixture was refluxed for 1 d. The resulting brown solution was taken to dryness by a Rotavapor and the dark oil treated with diethyl ether (5 cm^3). After separation of a brown solid (starting material; 10 mg, 0.013 mmol) the red-brown solution was rotoevaporated and the oily solid taken up in ethanol (2 cm^3). Upon addition of hexane (5 cm^3) the ethanol solution eventually gave a red-brown solid. Yield 26 mg, 60%.

[Re(NPh)Cl$_3$(H$_2$dpa)] 3. To a suspension of [Re(NPh)Cl$_3$(PPh$_3$)$_2$] (127 mg, 0.14 mmol) in benzene (10 cm^3) was added H$_2$dpa (39 mg, 0.14 mmol) and the mixture was refluxed for 12 h. The pale green precipitate was filtered off, washed twice with aliquots of benzene (1.5 cm^3) and diethyl ether (3 cm^3) and dried under vacuum. Yield 71 mg, 77% (Found: C, 43.9; H, 3.1; N, 4.2. $C_{24}H_{21}Cl_3N_2PRe$ requires C, 43.61; H, 3.20; N, 4.24%). The complex is soluble in dichloromethane, chloroform and dimethylformamide, insoluble in all other polar and non-polar solvents. FAB$^+$ mass spectrum: *m*/*z* 661 ([*M* + H]$^+$, 20), 626 ([*M* − Cl]$^+$, 50) and 591 ([*M* + H − 2Cl]$^+$, 100%). UV/VIS: λ_{max} 791 (ε 100) and 315 nm (11 700 dm^3 mol^{-1} cm^{-1}).

[Re(NPh)Cl(Hdpa)(H$_2$dpa)][ClO$_4$] 4. The complex [Re(NPh)Cl$_3$(PPh$_3$)$_2$] (32 mg, 0.035 mmol) was suspended in MeOH (10 cm^3), solid H$_2$dpa (20 mg, 0.07 mmol) was added and the mixture refluxed for 3 h. The resulting brown solution was concentrated to half volume by a flux of nitrogen and NaClO$_4$ (12 mg, 0.1 mmol) in methanol (2 cm^3) was added. After 24 h, upon filtration, a dark crystalline solid was recovered, washed with methanol (2 cm^3) and diethyl ether (3 cm^3). Yield 18 mg, 55% (Found: C, 52.3; H, 3.5; N, 4.2. $C_{42}H_{34}Cl_2N_3O_4P_2Re$ requires C, 52.33; H, 3.55; N, 4.36%). The complex is soluble in dichloromethane, chloroform (with decomposition), acetone, acetonitrile and ethanol, slightly soluble in methanol and benzene and insoluble in diethyl ether and hydrocarbons. Molar conductivity in MeCN: $\Lambda_M = 108\ \Omega^{-1}$ cm^2 mol^{-1} (1 : 1 electrolyte). FAB$^+$ mass spectrum: *m*/*z* ([*M* − Cl]$^+$, 100%). UV/VIS: λ_{max} 585 (ε 4300), 473 (5500), 436 (6000) and 333 nm (13 100 dm^3 mol^{-1} cm^{-1}).

[Re(NPh)(OEt)(dppd)] 5. In a round-bottomed flask solid [Re(NPh)Cl$_3$(PPh$_3$)$_2$] (63 mg, 0.07 mmol) and solid H$_2$dppd (42 mg, 0.07 mmol) were mixed, and alkaline [by NEt$_3$ (707 mg, 7 mmol)] ethanol solution (15 cm^3) added. The mixture was refluxed for 3 h and the red-violet solution concentrated to 5 cm^3. The dark precipitate was filtered off and washed twice with ethanol (2 cm^3) and diethyl ether (4 cm^3). Yield 56 mg, 88% (Found: C, 62.8; H, 4.9; N, 4.4. $C_{47}H_{44}N_3OP_2Re$ requires C,

Table 3 Comparison of the Re=N–C moieties in phenylimidorhenium complexes

Compound	Oxidation state	Geometry about Re	Re=N/Å	Re=N–C/°	Ref.
$[Re(NPh)Cl_3(PPh_3)_2]\cdot CH_2Cl_2$	V	Octahedral	1.726(6)	172.6(6)	19
$[Re(NPh)(OEt)(bipy)_2]^{2+}$	V	Octahedral	1.740(6)	167.4(6)	20
$[Re(NPh)L_2(PPh_3)]^{+}$ [a]	V	Octahedral	1.709(8)	165.5(5)	21
1	V	Octahedral	1.736(9)	175.4(9)	Present work
2	V	Octahedral	1.72(2)	168(2)	Present work
5	V	Octahedral	1.74(1)	172(1)	Present work
$[Hg(ReL_3)_2]$ [b]	V	Trigonal planar	1.76(1)	173(1)	22
$[N(PPh_3)_2][ReL_3]$ [b]	V	Trigonal planar	1.60(1) 1.753(8) 1.684(9)	168.8(8) 173.6(8) 173.2(8)	23
$[ReL_3Ph]$ [b]	VII	Tetrahedral	1.754(6)	164.9(4)	24
$[ReL_3(OSiPh_3)]$ [b]	VII	Tetrahedral	1.740(3)	167.6(3)	24
$[ReL_3(OSiPh_3)]$ [c]	VII	Tetrahedral	1.753(5)	157.5(3)	24
$[ReL(CHBu^t)(OC_6H_3Cl_2\text{-}2,6)_3]$ [b]	VII	Square pyramidal	1.74(1)	168(1)	25
$[ReL(CHBu^t)(OC_6F_5)_3(thf)]$ [b]	VII	Square pyramidal	1.724(5)	173.0(5)	25
$[ReL_2Me(CH_2Bu^t)_2]$ [a]	VII	Trigonal bipyramidal	1.751(2)	175.2(2)	26
$[ReL_2Cl_3Me]^{-}$ [c]	VII	Octahedral	1.723(4)	169.8(5)	26

[a] L = 3-hydroxy-2-methyl-(4*H*)-pyran-4-onate. [b] L = $NC_6H_3Pr^i{}_2$-2,6. [c] L = $NC_6H_3Me_2$-2,6.

Table 4 Structure determination summary for complexes **1**, **2** and **5**

	1	**2**	**5**
Empirical formula	$C_{43}H_{38}N_3OP_2Re$	$C_{42}H_{35}ClN_3P_2Re$	$C_{47}H_{45}N_3O_{1.5}P_2Re$
M	860.9	865.3	924.0
Color, habit	Dark red parallelepipeds	Black parallelepipeds	Dark red parallelepipeds
Crystal size/mm	0.10 × 0.30 × 0.30	0.08 × 0.10 × 0.08	0.15 × 0.20 × 0.30
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pnma*	$P2_12_12_1$	$P\bar{1}$
a/Å	11.816(4)	10.178(4)	11.307(4)
b/Å	21.028(7)	17.680(6)	13.333(6)
c/Å	15.085(4)	20.254(7)	27.743(11)
α/°			88.64(3)
β/°			80.65(3)
γ/°			79.48(3)
U/Å^3	3748(2)	3645(2)	4058(3)
D_c/Mg m^{-3}, *Z*	1.53, 4	1.58, 4	1.51, 4
μ/mm^{-1}	3.4	3.5	3.1
F(000)	1720	1720	1860
2θ Range/°	4.5–50.0	4.0–40.0	4.5–50.0
Scan speed/° min^{-1} in ω	Variable; 1.50 to 14.65	Variable; 3.50 to 14.65	Variable; 2.49 to 14.65
Index ranges	$0 \leqslant h \leqslant 14, 0 \leqslant k \leqslant 25,$ $0 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 9, 0 \leqslant k \leqslant 17,$ $0 \leqslant l \leqslant 19$	$0 \leqslant h \leqslant 12, \quad -15 \leqslant k \leqslant 15,$ $-32 \leqslant l \leqslant 33$
Independent reflections	3384	1964	9099
Observed reflections [$I_o \geqslant 2\sigma(I)$]	2590	1555	7612
Number of parameters refined	236	169	718
Final *R*, *wR*2 (observed data)	0.048, 0.130	0.044, 0.106	0.050, 0.145
Goodness of fit	1.186	0.779	0.97
Data-to-parameter ratio	11.0:1	9.2:1	10.6:1
Largest difference peak/e Å^{-3}	1.55 (0.77 Å from Re)	1.06 (1.11 Å from Re)	1.29 (0.85 Å from Re)

Details in common: Siemens R3m/V diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); 294 K; highly oriented graphite-crystal monochromator; ω–2θ scan type; scan range 0.70° + Kα separation; stationary crystal and counter at beginning and end of scan, each for 25% of total scan time; two standard reflections every 150; empirical ψ-scan method for absorption correction (XEMP program[31]); solution by heavy-atom methods; refinement on F^2; $w = [\sigma^2(F_o{}^2) + (aP)^2 + bP]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$.

61.69; H, 4.85; N, 4.59%). Crystals suitable for the X-ray determination were grown from a dichloromethane solution layered with ethanol. The complex is soluble in dichloromethane, chloroform (with decomposition), acetone, acetonitrile, slightly soluble in ethanol and methanol and insoluble in diethyl ether and hydrocarbons. FAB$^+$ mass spectrum: *m*/*z* 870 ([*M* − OEt]$^+$, 100%). UV/VIS: λ_{max} 493 (ε 7100), 428 (8700), 374 (11 000) and 274 nm (35 400 dm^3 mol^{-1} cm^{-1}).

[Re(NPh)Cl(Hdppd)]Cl 6. The complex $[Re(NPh)Cl_3(PPh_3)_2]$ (59 mg, 0.065 mmol) was suspended in acetonitrile (10 cm^3) and solid H_2dppd (39 mg, 0.065 mmol) added. The solution was stirred at reflux for 3 h then evaporated to an oil which, by treatment with diethyl ether and upon vigorous stirring, gave a red-violet precipitate. The solid was washed five times with aliquots (5 cm^3) of diethyl ether until the filtrate was colourless. Yield 52 mg, 88% (Found: C, 56.8; H, 4.4; N, 4.3. $C_{45}H_{40}ClN_3P_2Re$ requires C, 57.38; H, 4.28; N, 4.46%). The complex is soluble in dichloromethane, chloroform, methanol, ethanol, acetone and acetonitrile, slightly soluble in diethyl ether and insoluble in hydrocarbons. Molar conductivity in MeCN: Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). FAB$^+$ mass spectrum: *m*/*z* 871 ([*M* − Cl]$^+$, 60%). UV/VIS: λ_{max} 501 (ε 4500 dm^3 mol^{-1} cm^{-1}), 464 (sh) and 313 nm (sh).

Crystallography

The crystal data, intensity measurements and data processing for complexes **1**, **2** and **5** are summarized in Table 4. Cell parameters were determined from 50 high-angle data (2θ > 20°). The diffracting ability of sample **2** fell off rapidly with increasing Bragg angle, and much of the higher-angle data, preliminarily collected, were flagged as weak and bore negative intensity. As a consequence the data collection was restricted to $2\theta = 40°$. To ensure a good observation : variable ratio and to achieve convergence, for complex **2** only Re, Cl and P atoms were refined anisotropically. For **1** and **5** all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and constrained to ride on the atoms to which they are bonded. Their contributions were added to the structure-factor calculations but their positions were not refined. Difference maps, calculated after the refinement, were essentially featureless, apart from a relevant peak (up to 2.8 e $Å^{-3}$) in **5** attributable to the oxygen atom of a water molecule. For **2** the Flack[30] absolute structure parameter was close to zero [0.06(3)]. The SHELXTL PC and SHELXL 93[31] computer programs were employed for the solution and refinement of the structures.

CCDC reference number 186/862.

See http://www.rsc.org/suppdata/dt/1998/923/ for crystallographic files in .cif format.

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